UDC 666.762.856

COMPOSITES BASED ON ALUMINUM-SILICATE GLASS CERAMIC WITH DISCRETE FILLERS

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It is shown that composite materials (CM) can be synthesized on the basis of Sr-anortite glass ceramic with BN_{hex}, α-Si_3N_4, β-Si_3N_4 and TiC powders introduced as disperse fillers. It is shown that the mechanism and temperature range of sintering in obtaining CM are determined by the chemical composition and dispersity of the matrix glass powder, while the degree of compaction and the structure of the composite depend on the dispersity of the fillers, particle shape, particle proneness toward aggregation and wettability by the glass phase of the matrix. It is established that the introduction of BN_{hex} particles decreases the dielectric permittivity of the Sr-anortite glass ceramic. Silicon nitride powder increased the critical coefficient of intensity of the stresses in the matrix by more than a factor of 2.5. Reinforcement with TiC particles increases the elastic modulus and microhardness and decreases the coefficient of friction of CM compared with the initial glass ceramic.

Key words: composite materials, glass ceramic, strontium anortite, $SrO–Al_2O_3–SiO_2$, BN, TiC, Si_3N_4, disperse non-oxide fillers.

Advances in promising fields in technology, the chemical industry, aircraft and automobile manufacturing and power generation are impossible without new types of materials suitable for operation at high temperatures and pressures, under dynamic loads, in aggressive media, in high velocity gas and fluid flows and in the presence of other factors [1, 2].

One possible solution to this problem is to develop composite materials (CM) with the required complex of properties, corresponding to the operating conditions of assemblies and structures.

Composite materials with metal, polymer, glass, ceramic and glass ceramic matrices have now been developed. The first CM based on glass, ceramics and glass ceramics were obtained in the 1960s [3, 4]. They have demonstrated their substantial advantages over CM with metal and polymer matrices: low density, high mechanical properties combined with high operating temperatures, high heat resistance and thermal stability of phase composition, durability and resistance to aggressive media.

By virtue of the low viscosity of glass at temperatures 800 – 1400°C the use of glassy and glass ceramic matrices in the synthesis of composites makes it possible to obtain CM at lower annealing temperatures and with more complicated shapes as well as to prevent degradation of non-oxide fillers during the manufacturing process [2]. In addition, the presence of a glass phase during heat-treatment gives a medium for phase transformations and growth of the filler grains inside the matrix, thereby making it possible to obtain CM by an *in-situ* method. For example, composite materials based on a matrix in the barium-aluminum-silicate (BAS) system and Si_3N_4 whiskers have been synthesized. The transformation from the α- into the β-modification and growth of silicon β-nitride grains occurred directly during annealing of the material. As a result the formation of a complex bimodal microstructure of the composite giving high mechanical performance was observed [5].

The choice of the chemical composition of the matrix is one of the most important aspects of the development of CM and is determined by the functional purpose of the composite created. The chemical composition of the matrix imparts to composites, first and foremost, operational properties such as the working temperature, chemical stability and durability, dielectric properties, and others. In the development of CM for high-temperature applications matrices are chosen on the basis of refractory glasses in the borosilicate system with low

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TABLE 1. Physical-Mechanical Properties of Fillers

Filler	Properties						
	T_m, °C	CLTE, 10^{-7} K^{-1}	ρ, kg/m³	E, GPa	σ_b, GPa	ε^*	$\tan \delta \times 10^4$
BN$_{hex}$	3000	0 – 72	2340	47 – 74	0.103	4	5
α-Si$_3$N$_4$	1400 (transition into β-Si$_3$N$_4$)	28 – 32	3184	260 – 330	600 – 1200	7.9 – 8.14	6 – 17
β-Si$_3$N$_4$	1900	28 – 32	3187	260 – 330	600 – 1200	7.9 – 8.14	6 – 17
TiC	3067	74	4910	410 – 510	850	–	–

* At frequency 10 MHz.

CLTE such as Pyrex, Duran or aluminum-silicate glass compositions forming sitals, in which crystallization with precipitation of high-temperature crystalline phases occurs during heat-treatment. The most widely used glass ceramic matrices in the aluminum silicate system are: Li$_2$O–Al$_2$O$_3$–SiO$_2$ (LAS), CaO–Al$_2$O$_3$–SiO$_2$ (CAS), BaO–Al$_2$O$_3$–SiO$_2$ (BAS), MgO–Al$_2$O$_3$–SiO$_2$ (MAS) and combinations of these matrices, for example, MLAS and BMAS or strontium-celsian (BaO—SrO–Al$_2$O$_3$–SiO$_2$) [4].

The purpose of introducing fillers into glass and glass ceramic matrices is to increase their mechanical properties: strength, crack resistance, elastic modulus, microhardness, durability and others. Together with this the introduction of fillers depending on their composition, type and amount can affect matrix characteristics such as thermal stability, coefficient of friction, thermal conductivity, electric conductivity and other properties.

At the beginning stages in the development of CM based on glass and glass ceramics researchers focused on developing composites, reinforced with continuous fillers in form of fibers, twisted and untwisted filaments, strands (rovings), ribbons, fabric with different weave and so on. Work on strengthening glass ceramic matrices with carbon, silicon carbide and mullite continuous fibers was widely disseminated [3, 6].

Analysis of the scientific and patent literature showed that continuous fillers make it possible to attain a higher degree of hardening of elastic matrices than discrete fillers, but they are characterized by complexity and high cost of fabricating fillers and the composites based on them, which greatly limits their applications. In this connection, in the last few years researchers have been showing more and more interest in glass ceramic compositions (GCC) obtained using discrete fillers.

The first works on obtaining precipitation-hardened GCC involved the introduction of metallic fillers into glass: Ni, W, V, Mo, Cu, Al and alloys in the system Fe–Ni–Co in the form of particles or whiskers [3].

Recently, more and more attention has been devoted to ceramic fillers, such as plates, spheres, filaments, discrete fiber or particles of Al$_2$O$_3$ [7], ZrO$_2$ or Y$_2$O$_3$-stabilized ZrO$_2$ [8], SiC [9], C, TiC [10], Si$_3$N$_4$ whiskers or grains [5] and others. The content of the reinforcing phase in such composites, as a rule, varies from 30 to 55 vol.%. The great interest in ceramic fillers is due to their high physical-mechanical properties. In addition, the most interesting fillers are non-oxide refractory compounds — carbides and nitrides.

It should be noted that works on obtaining composites reinforced with several different fillers have appeared simultaneously in the last few years. For example, materials based on a BAS-glass ceramic matrix hardened by Si$_3$N$_4$ grains and short SiC$_{sf}$ (C$_{sf}$) fibers or α-SiC particles have been developed.

Even though definite advances have been made research, development work and industry adoption of new types of composites based on glass ceramic matrices, specifically, nano-composites reinforced with carbon nano-tubes, are actively continuing in the leading countries of the world.

The objective of the present work is to synthesis composites based on glass ceramic aluminum silicate matrix with finely dispersed non-oxide fillers and to determine any regularities in the effect of the nature, concentration and dispersity of fillers on the synthesis, structure and properties (microhardness, Young's modulus, crack resistance, durability, coefficient of friction) of the composites obtained.

EXPERIMENTAL PROCEDURE

The composition of glass in the system SrO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ was chosen as the matrix to obtain composites, since under heat-treatment monoclinic strontium anortite, which possesses a high melting temperature (1760°C), good mechanical properties ($E = 100$ GPa, $\sigma_b = 100 – 120$ MPa) and quite low CLTE [$(26 – 48) \times 10^{-7}$ K^{-1}], precipitates as the dominant crystalline phase [12].

The most promising filler for glass ceramic composites are high-temperature non-oxide compounds — nitrides or carbides, which include BN$_{hex}$, Si$_3$N$_4$ and TiC. These compounds possess a complex of valuable mechanical and physical-chemical properties (Table 1). Boron nitride possesses low dielectric characteristics [ε (10^6 Hz) = 4.15]. The use of silicon nitride will make it possible to increase crack resistance [5] and titanium carbide — hardness and strength [10, 13].

TABLE 2. Filler Characteristics

| Filler	Phase composition	Density, kg/m^3	Average particle size, μm	Particle shape
BN$_{hex}$	BN$_{hex}$	2320	3	Scaly
α-Si$_3$N$_4$	α-Si$_3$N$_4$, β-Si$_3$N$_4$	3180	7	Filamentary
β-Si$_3$N$_4$	β-Si$_3$N$_4$, α-Si$_3$N$_4$	3180	9	Elongated
TiC	TiC	4940	50	Continuous, close to spherical

Glass with SAS composition (wt.%) — 20 SrO, 30 Al$_2$O$_3$, 40 SiO$_2$ and 10 TiO$_2$ — was synthesized under oxidizing conditions at temperature 1600°C. The quenched cullet obtained by casting into water was comminuted in a planetary mill to dispersity 10 μm. Commercial powders of BN$_{hex}$, α-Si$_3$N$_4$, β-Si$_3$N$_4$ and TiC with particle sizes 2, 7, 9 and 50 μm, respectively, were used as fillers. On the basis of the published data, the filler content was 30 vol.%. The effect of the filler concentration was studied for composites reinforced with α- and β-Si$_3$N$_4$ in amounts from 30 to 70 vol.%.

The CM was obtained by hot pressing in graphite molds and argon medium in a FCT HPW S8401 (FCT Systeme GmbH Company) high-temperature press.

The main methods of investigation were laser granulometry (Analysette 22 NanoTec, MicroTec, Fritsch), differential scanning calorimetry (STA 449 C Jupiter, Netzsch), x-ray phase analysis (D2 Phaser, Bruker) and dilatometric determination of the shrinkage during heating in argon medium (DIL 402 PC dilatometer, Netzsch). The filler density was determined by helium pycnometry (AccuPyc 1340, Micromeritics). The modulus of elasticity, microhardness, crack resistance and coefficient of friction were chosen as the main indicators of the mechanical properties. The elastic modulus and microhardness were measured by means of nano-indentation in a Nanohardess Tester, CSM Instruments. The crack resistance of the materials was determined in a DuraScan 50 microhardness testing machine with an Emco-test optical attachment. A complex tribological study of the samples included continuous recording of the coefficient of friction (CF) with wear testing using the rod – disk scheme on an automated setup Tribometer, CSM Instruments. The microstructure of the materials was analyzed using a microprobe system based on a JSM-6480LV Jeol scanning electron microscope. The ceramic and dielectric properties were studied in accordance with the procedures adopted and state standards.

RESULTS AND DISCUSSION

The density, phase composition, shape and predominant particle size were determined for the fillers used (Table 2).
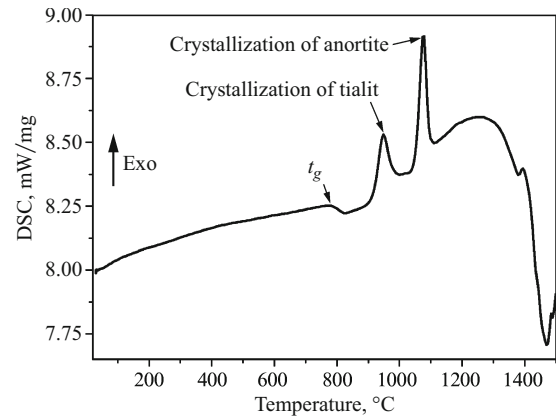
Fig. 1. DSC results for the initial glass powder.
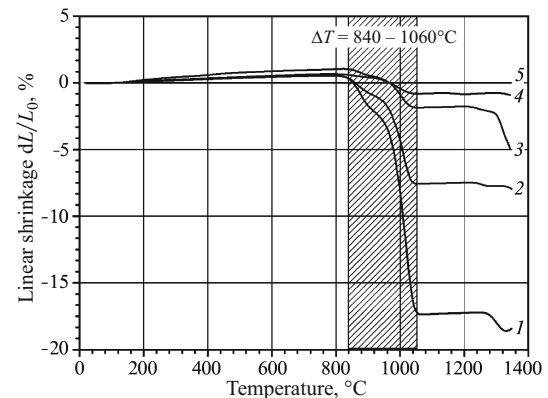
Fig. 2. Continuous shrinkage curves for the samples, obtained in a high-temperature dilatometer in argon medium: *1*) SAS, *2*) SAS/β-Si$_3$N$_4$, *3*) SAS/BN, *4*) SAS/TiC, *5*) SAS/α-Si$_3$N$_4$.

To determine sintering regimes of the experimental glass powder with different fillers the physical-chemical processes occurring when glass powder is heated were studied (Fig. 1) and the continuous shrinkage curves for pressed samples during heating in argon medium were obtained (Fig. 2). Comparing the data obtained showed that the materials sinter in the temperature range 840 – 1060°C by the viscous flow mechanism on account of the softening of the glass phase. Compaction stops in the interval 1060 – 1300°C, which is explained by the crystallization of the glass with precipitation of crystalline phases — tialit and monoclinic strontium anortite.

On the basis of an analysis of the DSC and continuous shrinkage curves obtained for the samples, a two-step hot-pressing regime with soakings at 970 and 1100°C was chosen to synthesize CM. On the one hand this regime made it possible to obtain a dense composite with low porosity while on the other hand the crystallization of the glass phase and formation of a glass ceramic occurred at a finite temperature.

The hot-pressing pressure was 30 MPa. The materials obtained were characterized by relative density 90 – 97% de-
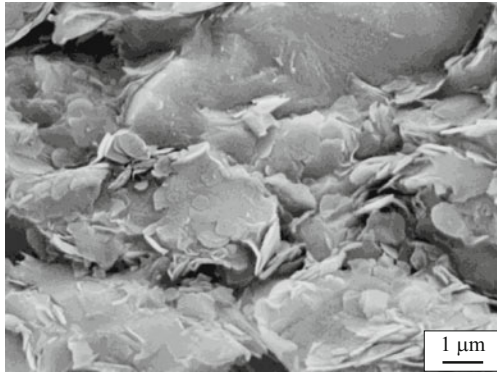
Fig. 3. Electron microscopy of the composite SAS/BN$_{hex}$.

Fig. 4. Relative density of the composites SAS/α-Si$_3$N$_4$ and SAS/β-Si$_3$N$_4$ versus the filler content.

pending on the nature of the filler (Table 3). According to the XPA data (see Table 3), depending on the nature of the filler the predominant phases in the synthesized composites were BN$_{hex}$, α-Si$_3$N$_4$, β-Si$_3$N$_4$, TiC and monoclinic strontium anortite. Electron microscopy of the samples (see Fig. 3) showed that the materials obtained are characterized by a fine-crystalline structure with a uniform filler distribution in the matrix and the absence of degradation during annealing.

Analysis of the data obtained attests that the temperature interval and mechanism of sintering of the glass powders with fillers are determined by the temperature interval and mechanism of sintering of the glassy matrix and therefore by its chemical composition and dispersity. The refractory non-oxide fillers chosen are inert with respect to the oxide matrix and inactive to sintering at temperatures to 1300°C and they do not change the phase formation process in the initial glass ceramic.

The effect of the fillers is manifested in a decrease of the degree of compaction attained during sintering, which is confirmed by the decrease in the magnitude of the finite shrinkage of the glass ceramic in the series β-Si$_3$N$_4$, BN$_{hex}$, TiC and α-Si$_3$N$_4$. The filler particles form a framework in the material, thereby increasing the apparent viscosity of the system, i.e., they fulfill the role of a reinforcing phase. In the process,

the sintering occurring by the mechanism of viscous flow of the glass phase is impeded. The dispersity, particle shape, proneness toward particle aggregation and wettability by the strontium-aluminum-silicate glass phase determine the degree to which the fillers affect compaction.

Two series of composites containing α-Si$_3$N$_4$ and β-Si$_3$N$_4$ with content 10 – 70 vol.% were synthesized to study the effect of the filler concentration on the sintering of the materials. The samples were hot-pressed using a two-step regime. It was determined that the final density of the materials decreases with increasing filler fraction (Fig. 4). It follows from the data that when using hot-pressing the maximum volume content of the filler should not exceed 30%. The morphology of the crystals also plays a large role. Thus, composites sinter to a denser state with silicon β-nitride than α-Si$_3$N$_4$. This could be due to the different shape of the filler particles. α-Si$_3$N$_4$ powder comprised aggregates consisting of small filamentary crystals, which complicated the penetration of the softened glass phase of the matrix in the intergrain space and, therefore, the healing of pores during sintering. This is confirmed by the loose microstructure of the composite with a nonuniform filler distribution in the matrix and the residual pores between the α-Si$_3$N$_4$ crystals (Fig. 5a). In addition, it was determined that β-Si$_3$N$_4$ possesses better wettability by the strontium-aluminum-silicate glass phase, as the formation of dense contacts between the matrix and the filler grains in the EM photographs (Fig. 5b) attest.

The hardness, Young's modulus and crack resistance of the composites obtained were determined. The method of nano-indentation and a DuraScan 50 microhardness testing machine with an optical attachment were used for this.

The values obtained for the mechanical properties of the materials are presented in Table 4, from which it follows that the introduction of all fillers increases the elastic modulus, and TiC, for which a large increase of the microhardness is also characteristic, increases Young's modulus the most. This is because TiC particles, possessing good wettability by and high adhesion to the glass matrix, made it possible to obtain a high-density composite, while the high values of the elastic modulus and microhardness of TiC ($E = 410 – 510$ GPa and $H = 28 – 35$ GPa) led to high mechanical properties of the

TABLE 3. Phase Composition and Ceramic Properties of the CM Obtained

Material	Phase composition	Open porosity, %	Relative density, %
SAS	SrAl$_2$Si$_2$O$_8$, Al$_2$TiO$_5$	0.1	99.9
SAS/BN$_{hex}$	BN$_{hex}$, SrAl$_2$Si$_2$O$_8$	7	92
SAS/α-Si$_3$N$_4$	α-Si$_3$N$_4$, SrAl$_2$Si$_2$O$_8$	8	90
SAS/β-Si$_3$N$_4$	β-Si$_3$N$_4$, SrAl$_2$Si$_2$O$_8$	0.2	94
SAS/TiC	TiC, SrAl$_2$Si$_2$O$_8$	0.4	97

TABLE 4. Mechanical and Dielectric Characteristics of Composites based on Aluminum-Silicate Glass Ceramic

Filler	Filler content, %[*]	E, GPa	H_V, GPa	K_{1C}, MPa $\cdot$ m$^{1/2}$	ε[**]	tan δ[**]
No filler	0	79 ± 8	9.2 ± 1.5	2.4	8.15	0.010
BN$_{hex}$	30	–	–	–	6.73	0.016
α-Si$_3$N$_4$	30	103 ± 27	9.3 ± 4.3	6.7	–	–
β-Si$_3$N$_4$	30	95 ± 12	8.6 ± 1.2	5.9	–	–
TiC	30	136 ± 70	12.2 ± 6.3	3.5	–	–

[*] By volume.

[**] At frequency 10^{10} Hz.
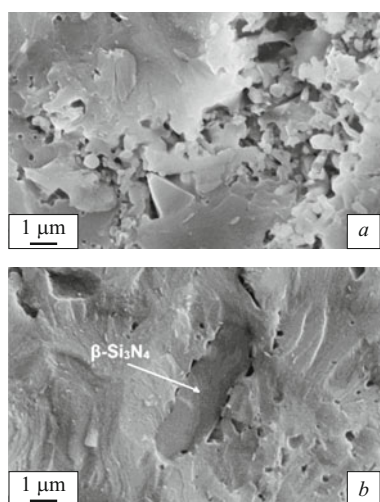
Fig. 5. Electronic photographs of composites containing 30 vol.% filler: α-Si$_3$N$_4$ (*a*) and β-Si$_3$N$_4$ (*b*).

composite obtained compared with the initial glass ceramic. In addition, it was shown that this filler increases the durability of the composite and lowers it coefficient of friction with steel (100 Cr6) from 0.57 to 0.41. However, the large size and spherical shape of the filler particles made it impossible to increase the crack resistance of the composite significantly. The large increase of K_{1C} by more than a factor of 2.5 is observed for CM with α- and β-forms of silicon nitride owing to the high values of their mechanical properties, high dispersity and large particle length to diameter ratio.

An investigation of the dielectric characteristics at frequency 10^{10} Hz of the composite with boron nitride showed a significant decrease of the dielectric constant ε from 8.15 for the initial glass ceramic to 6.73 for the composite, the change in the dielectric characteristics not exceeding 3% in the temperature interval 20 – 1100°C.

In summary, it was found that composites can be synthesized on the basis of Sr-anortite glass ceramic with BN$_{hex}$, α-Si$_3$N$_4$, β-Si$_3$N$_4$ and TiC introduced as fillers. It was shown that the mechanism and temperature interval of sintering in obtaining composite materials are determined by the chemical composition and dispersity of the matrix glass powder, while the degree of compaction and the structure of the composite depend on the filler dispersity, particle shape, particle proneness toward aggregation and wettability are determined by the glass phase of the matrix. It was determined that the introduction of particles of BN$_{hex}$, owing to the low values of its dielectric characteristics, decreases the dielectric permittivity of the strontium-anortite glass ceramic. Silicon nitride powders can be used to increase the value of the critical coefficient of stress intensity of the matrix by more than a factor of 2.5. Reinforcement with TiC particles increases the elastic modulus and microhardness and decreases the coefficient of friction of the composites compared with the initial glass ceramic.

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